CCXXIII.—*Cadmium and Beryllium Peroxides.*

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ALL the metals of Group II of the periodic table have been shown to form peroxides of the formula MO_2 (zinc in the form $ZnO_2,\frac{1}{2}H_2O$) with the exception of cadmium and beryllium, whose peroxides would indeed be expected to be less stable than the others. Many so-called peroxides of cadmium have been prepared containing active oxygen ranging from $CdO_{1\cdot5}$ to $CdO_{1\cdot8}$ (Haas, *Ber.*, 1884, **17**, 2253; Kruss, *ibid.*, p. 2595; Kuriloff, *Ann. Chim. Phys.*, 1891, **23**, 430; Manchot, *Ber.*, 1906, **39**, 1170; Eijkman, *Chem. Zentr.*, 1905, I, 1628), but only a little work has been done on beryllium peroxide, Komarovsky (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 608) having obtained some basic peroxides.

Accordingly, it was decided to make and compare the peroxides of cadmium and beryllium.

Preparation and Examination of Cadmium Peroxide.—(1) A method was sought in which cadmium hydroxide could be obtained in solution and submitted to mild oxidation by hydrogen peroxide. Unlike baryta, cadmium hydroxide was found to be insoluble in sucrose solution, but it dissolved slowly in a concentrated solution of ammonium nitrate, and when this solution was added to 30% hydrogen peroxide a cream precipitate was obtained in small yield; this was washed free from hydrogen peroxide and dried in a vacuum desiccator over phosphoric oxide. It decomposed explosively into cadmium oxide and oxygen on heating.

Analysis. Cadmium oxide was determined by simple ignition. Ammonium nitrate, which the preparation was found to contain, could be roughly estimated by a preliminary gentle ignition. The "active" oxygen was determined by dissolving a sample in ice-cold dilute sulphuric acid, containing boric acid, and titrating with standard potassium permanganate solution. (Nitric acid may be used in place of the sulphuric acid.) A specimen analysis showed CdO 80·0, active oxygen 7·42, NH_4NO_3 7·0%. The remaining 5—10% in the preparations was assumed to be water, the presence of which was demonstrated.

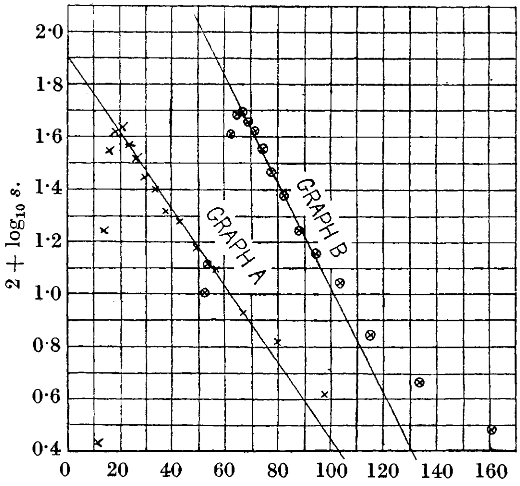
In the preparations, the method of addition of the reagents, excess of hydrogen peroxide, concentration of cadmium solution, and the temperature were varied, yet the ratio CdO : O remained constant (1·66, 1·72, 1·74, 1·73) corresponding to Cd_3O_5. Moreover, the water content could be decreased by longer desiccation; for instance, after 9 days the ratio H_2O : O (active) was 0·73 : 0·66, but another preparation dried for a month gave a ratio 0·47 : 0·72. Hence, the peroxide was not a compound of hydrogen peroxide and may therefore be formulated Cd_3O_5,xH_2O. The substance was quite stable, the percentage of active oxygen showing no change after a month.

(2) To avoid the hydrolysis possible in Method 1, alcoholic potash was added to an alcoholic solution of cadmium bromide containing perhydrol; the resulting white precipitate was washed free from potassium bromide and then corresponded to $CdO_{1\cdot62}$.

(3) By adding a solution of cadmium hydroxide in ammonia to perhydrol, a pale cream precipitate was obtained which was dried and analysed as before. The proportion of oxygen remained constant whilst the concentrations of the reacting solutions and the excess of hydrogen peroxide were changed within wide limits, and

corresponded to Cd_4O_7. Ammonium chloride was present. The water was always in too small quantity (about 6%) compared with the oxygen to correspond with a compound of hydrogen peroxide, and the *compound* could be formulated $Cd_4O_7,2H_2O$, *i.e.*, it is a "true" peroxide.

(4) The general method for preparation of metallic peroxides consisting in the addition of ethereal hydrogen peroxide to the metal alkyl in ethereal solution (Ebler and Krause, *Z. anorg. Chem.*, 1911, **71**, 150) was used, the cadmium dimethyl being prepared from the Grignard reagent (Krause, *Chem. Zentr.*, 1918, I, 177). The resulting cream precipitate was washed with dry ether and dried; it was more explosive on heating than the previous preparations.



Time, *t*, in minutes.

(*For Graph B,* 50 *has been added to each time reading.*)

Analysis. Besides cadmium oxide and active oxygen, the preparation contained water and a little carbon dioxide, the last two constituents being determined by heating in a stream of nitrogen (Found : CdO 83·16, active O 7·10, water 7·41, CO_2 2·61 ; total 100·28%). The concentrations of the reacting ethereal solutions, their temperature, and the excess of hydrogen peroxide were varied, but the proportion of active oxygen was not affected (*e.g.*, CdO : O = 1·74, 1·70, 1·71, 1·76, 1·69) and corresponded to Cd_3O_5. A low temperature merely caused a slow precipitation. When the cadmium dimethyl was dissolved in a mixture of absolute alcohol (1 vol.) and ether (1 vol.) the apparently similar precipitate exploded violently on being dried in a vacuum desiccator. Two preparations were carried out in an atmosphere of dry nitrogen. The water content, sometimes in excess of that required to form hydrogen peroxide with the active oxygen, was never insufficient for that purpose. This shows that we may formulate the *compound* as $3CdO,2H_2O_2$, *i.e.*, that it is not a "true" peroxide. This result is in accordance with the decreased stability of the preparation.

(5) Small quantities of peroxide were produced by passing ozone through a suspension of finely divided brown cadmium oxide in chloroform, a white deposit being formed. Blank experiments on the chloroform gave no hydrogen peroxide.

Other methods. The electrolysis of cadmium chloride with hydrogen peroxide in the cathode chamber produced cadmium hydroxide. The addition of potassium hydroxide to cadmium chloride solution containing hydrogen peroxide, and secondly, the pouring of a solution of potassium hydroxide, cadmium chloride, and Rochelle salt into perhydrol gave only gelatinous precipitates.

The Velocity of Thermal Decomposition of Cadmium Peroxides.— Still further to illustrate the constitution of the peroxides, their rate of thermal decomposition was examined. If two apparently distinct peroxides were both only different mixtures of, say, CdO_2 and CdO, their velocities of decomposition should give identical coefficients.

The rate of decomposition of the peroxide in an atmosphere of oxygen at atmospheric pressure was determined by measuring the oxygen evolved in a gas burette, the peroxide being kept at a constant temperature in a vapour bath. The levelling of the mercury was done accurately with the help of a sulphuric acid manometer; also a phosphoric oxide drying tube was inserted before the gas burette, and a smaller one just above the tube in which the peroxide was sealed. The large drying tube, manometer, and gas burette were finally all immersed in a cylinder of water to protect them from sudden changes of temperature and were connected to the reaction tube by thick-walled capillary tubing.

Peroxides from Method 4 were found to decompose unimolecularly (characteristic of a heterogeneous reaction) since a straight line was obtained by plotting the logarithm of the velocity (in c.c. of oxygen at *N.T.P.* per min.) against the time. The velocity coefficients were obtained from the graphs by measuring their slope and using the relation $k = 2{\cdot}30(\log_{10}s_1 - \log_{10}s_2)/(t_2 - t_1)$, s_1 and s_2 being the velocities at times t_1 and t_2. Thus, in the case of Graph A we find $k = 2{\cdot}30 \times 0{\cdot}0146 = 0{\cdot}0335$ (min.$^{-1}$). Similarly, other experiments gave the values 0·0336, 0·0322, and 0·0335. The temperature employed was 128°, amyl alcohol being used in the vapour bath.

Peroxides from Method 3 were similarly examined and found to be much more stable, although they contain more oxygen. This supports the conclusions previously reached with regard to their structure (*i.e.*, that they are " true " peroxides). At 156° (bromobenzene being used in the boiler) they decomposed unimolecularly. For example (see Graph B), we find $k = 2{\cdot}30 \times 0{\cdot}0202 = 0{\cdot}0465$. The values 0·0326, 0·0463, 0·0373 were similarly obtained.

The points on the left of the graphs correspond to the commencement of the reaction, those on the right to a period when the reaction has become extremely slow (say, 0·05 c.c. of oxygen per min.).

Beryllium Peroxide.—Method 4, which had been found most convenient for cadmium, was used with both beryllium dimethyl and diethyl. The addition of hydrogen peroxide to the beryllium alkyl solution in ether produced a gelatinous precipitate in the first case (dimethyl) and a brown coloration and then a solid in the second (diethyl). These precipitates gave no hydrogen peroxide with dilute acid.

Summary.

(1) Cadmium peroxides have been prepared and shown to correspond to the formulæ Cd_3O_5,xH_2O; $Cd_4O_7,2H_2O$; and $3CdO,2H_2O_2$.

(2) The last two were shown to decompose unimolecularly.

(3) Cadmium oxide can be peroxidised by ozone at ordinary temperatures.

(4) The alkyl method of preparation failed to give a peroxide with beryllium.

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